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PHOTOINDUCED CHANGES OF STRUCTURE AND PROPERTIES OF AMORPHOUS BINARY AND TERNARY CHALCOGENIDES

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New results obtained recently in the study of isotropic photoinduced effects are described and discussed. The isotropic effects in binary systems such as As-S, Sb-S and in some ternary systems (As-Ga-S, As-Sb-S, Ge-Sb-S, Ge-Ga-S) are connected with the changes of bond statistics and short range order not only in the case of irreversible changes but also in the case of reversible ones. Similar changes of optical properties and the structure that are produced by photodarkening can be obtained by change of stoichiometry of a film. It supports the idea that the exposure of such systems creates bonds among like atoms by photolytic reactions. The exposure influences also index of refraction. The present or potential applications of isotropic photoinduced effects for production of optical and optoelectronics elements and optical storage are also described and discussed.

1. Introduction

Photoinduced changes of structure and properties of amorphous chalcogenides have been the focus of many laboratories for many years because of their present and potential applications in optoelectronics (photoresists, optical storage, optical waveguides, optical gratings and other elements, optical circuits etc. (see, e.g. recent papers [1-6] and papers cited in)). Photoinduced effects have been studied intensively also in order to describe and understand these interesting phenomena [7-20].

Photoinduced changes of optical transmittivity and reflectivity, of index of refraction, changes of reactivity, of rates of diffusion and inter-diffusion, of viscosity and of the state (phase) have been observed in many materials, e.g. in a-Se [17, 19], in the systems of As-S, As-Se, As-Te, As-S-Te, Ge-S, Ge-Sb-S, Ge-Ga-S, Ge-Se, Ge-Sb-Se, Ge-Sb-Te, Ge-In-Te etc. [1-16, 18, 20-32]. In spite of the fact that large effort was given to this subject and several models for the description of individual photoinduced changes has been proposed, the mechanism of many photoinduced processes is still unclear [8,11,13-17, 20-22, 25-30]. Such a situation is partly caused by the fact that the photoinduced phenomena are apparently numerous and this term covers several effects with different mechanisms (changes of short-range-, medium-range- and long-range- orders, photolysis, photosynthesis, photoinduced oxidation, photoenhanced dissolution, diffusion and inter-diffusion, changes of reactivity, viscosity, polarization and anisotropy, vectoral effects, see e.g. [8, 18-20, 28-32]). In our view, the microscopic mechanism of all these effects cannot be the same. Even more, some of the photoinduced changes are relatively small (e.g. changes of medium-range order, some vectoral effects etc.), and their unambiguous determination and explanation is difficult.

In this paper, we will confine ourselves to scalar photostructural changes. New results will be presented and the papers published on this subject in recently will be discussed. Broader group of materials (e.g. As_2S_3, As-S and Sb-S systems, As-Sb-S, As-Ga-S, Ge-S, Ge-Sb-S and Ge-Se) will be discussed in order to support the elucidation of a model of these phenomena and to contribute to find new (or better) systems, properties or larger effects. At the end, present or possible applications of these phenomena will be mentioned.

2. Photoinduced effects

The interaction of amorphous chalcogenides with light is generally complex. The first step in all effects is the electronic excitation by exposure. In the second step, the excited state can relax to the original one, or to an electronic and atomic structure, which is different from the original. In the first case, the changes are temporary, in the second case the new state can be stable for a longer time. In evaporated films, the light can promote changes of electron densities, but also induce chemical reactions among fragments [29, 30]. It can also induce other photochemical reactions such as polymerization or depolymerization, photolysis, changes of local structure, changes of long-range order (crystallization - amorphization) [11, 19, 28-33]. These processes can proceed separately or simultaneously and in amorphous solids are enabled by two factors:

a) The first one is the large free volume of glasses [11, 31] (and no free volume in the crystals). The free volume of amorphous thin films is even larger than that of glasses due to the larger disorder. The free volume can be inversely proportional to the ω [11, 31]

$$\omega = [M - S]\delta = [M - S]\left[\rho \frac{\sum (A_i x_i / \rho_i) - \sum (A_i x_i / \rho)}{\sum A_i x_i} \right], \tag{1}$$

where [M − S] represents the density of M-S bonds, δ reflects the compactness of the structure. The A_i, x_i, ρ_i stand for atomic weights, atomic fraction and densities of the i-th element of the glass, respectively. The quantity ρ is the experimentally found density of the glass. In many amorphous systems, the largest photoinduced changes were found for compositions with the largest "free volume" (Fig. 1, [11, 29-31]).

b) The second positive factor for the evolution of photoinduced changes of structure in a-chalcogenides is generally a low coordination number (N_c) of chalcogens (mostly $N_c \cong 2$), and of pnictogens, (e.g. $N_c(As) \cong 3$), which makes the structure flexible. The largest photoinduced effects were found in our experiments in the As-S system for $As_{42}S_{58}$ films ($N_c = 2.42$), and in Ge-As-S films for $N_c = 2.67$ [11, 31].

2.1. Irreversible photoinduced changes

In several recent papers [7-11, 18, 21-23, 29-31], the irreversible and reversible photoinduced scalar phenomena in the model As-S system but also in Sb-S, As-Sb-S, Ge-Sb-S, Ge-Ga-S and other systems have been studied. The mechanisms of irreversible photoinduced changes in such systems are relatively well understood (see, e.g. [7, 8, 18, 25, 29, 30, 32]). During the high temperature vacuum evaporation of compounds or alloys or during their sputtering, which are the most common ways of preparation of their thin films, the starting materials are often thermally dissociated to fragments of original material. When the vapors are condensed on a cold substrate, the backward synthetic chemical reactions among the fragments to the original compounds (alloys) are not quick enough and the high-temperature state is then partly or fully frozen in and preserved. A micro-heterogeneous film, which is far from thermodynamic equilibrium, is then obtained.

For example, in as-evaporated films of the As-S system large amounts of As_4S_4 and S_n molecules are present (Figs. 2-4, bands between 120-260 cm^{-1} and bands with maxims near 345, 352, 361 cm^{-1} for As_4S_4 vibrations, and a band near 495 cm^{-1} for S-S vibrations (Figs. 2, 3) [8, 9, 29]). Exposure of such films can promote (or increase the rates of) chemical reactions among individual fragments of the film. This process accompanied by decrease of amplitudes of bands with maximum near 137, 148, 170, 193, 215, 223, 361, 495 cm^{-1}. The film is then homogenized and also polymerized. Its state becomes closer to the target glass and to thermodynamic equilibrium. (Figs. 2-4). This process of homogenization on atomic level goes even further when the films are annealed. The Raman bands corresponding to vibrations of As-As and S-S- bonds and vibration modes of As_4S_4 structural units (see above) are according to their composition ceasing or lowering their amplitudes. After thermal annealing of as-evaporated films, their structure approaches the structure of the original bulk glass (Figs. 2-4).
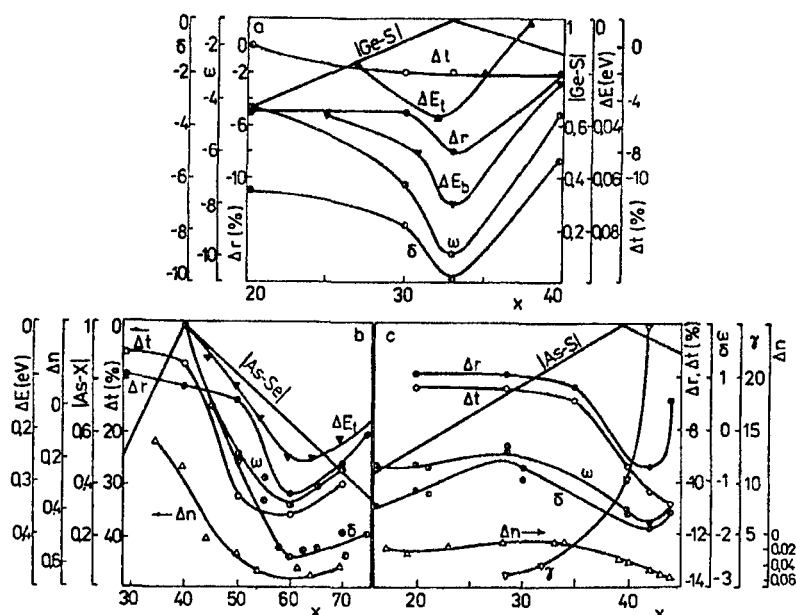
Fig. 1. Compositional dependence of optically induced changes of transmittivity, Δt, of thin films (d = 1 μm) and reflectivity, Δr, of powdered glasses of Ge_xS_{100-x} (a), As_xSe_{100-x} (b), and As_xS_{100-x} (c) systems [32]. The ΔE stands for photoinduced changes of absorption edge position of annealed bulk samples ($ΔE_b$) and thin films ($ΔE_t$), Δn stands for photoinduced changes of index of refraction. The quantity γ stands for the ratio of dissolution rates of exposed and unexposed films. The |M-X| are the densities of heteropolar bonds which might be changed by incident light (M = Ge, As; X = S, Se). The ω and δ are given by Eq. 1.

The difference between Raman spectra of the as-evaporated film after their annealing or after their exposure is mainly in amplitude of the band of As-As vibrations (235 cm^{-1} [20, 29, 30]), which is increased relatively to other bands after exposure (Figs. 2-4) due to photochemical reactions that will be discussed later. The exposure produces also photolysis.
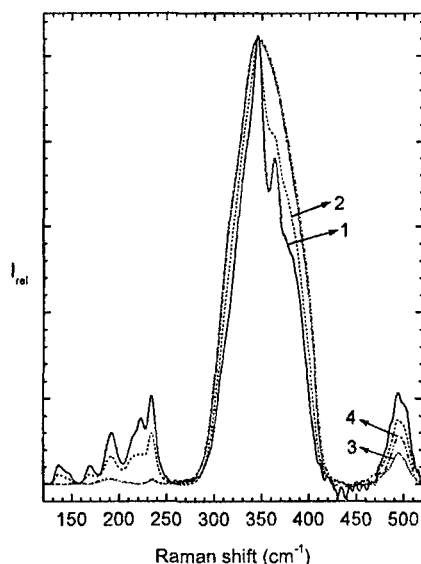

Raman shift (cm^{-1})

Fig. 2. Reduced Raman spectra of $As_{38}S_{62}$ thin films and bulk glass. 1: as-evaporated film, 2: exposed film, 3: annealed film, 4: bulk glass. The curves 3 and 4 are overlapping in the spectral region up to 270 cm^{-1}. Some narrow bands of the spectrum (130-250 cm^{-1}, 361 cm^{-1}) can be assigned to As_4S_4 molecules (see Fig. 5), the band 235 cm^{-1} can be assigned to As-As bonds vibrations [20], the band 495 cm^{-1} to S-S bonds vibrations [20, 24].
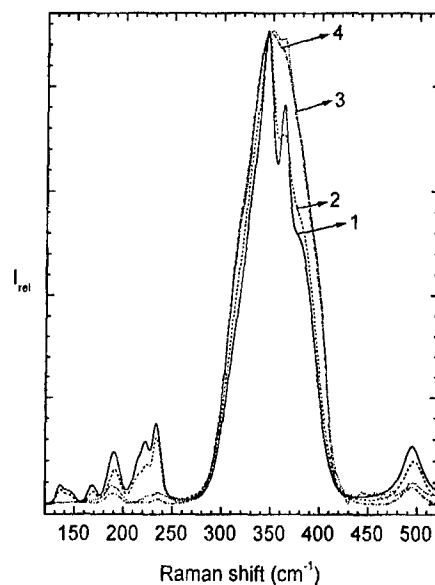
Fig. 3. Reduced Raman spectra of $As_{40}S_{60}$ thin films and bulk glass. _1:_ as-evaporated film, _2:_ exposed film, _3:_ annealed film, _4:_ bulk glass. For assignment see Fig. 2. The amplitudes of 495 cm^{-1} band (S-S vibrations) are lower than in S-rich films of $As_{38}S_{62}$ in Fig. 2.
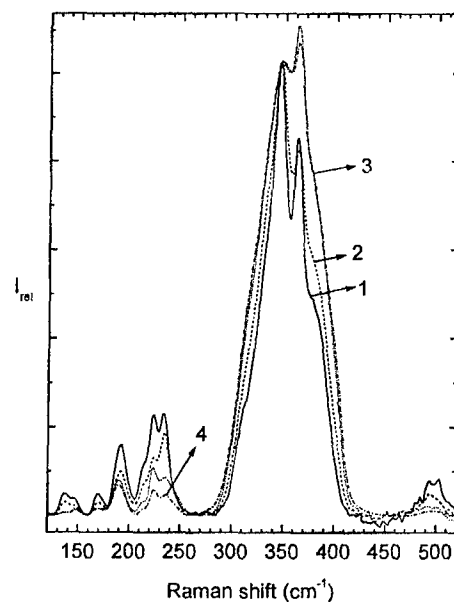

Fig. 4. Reduced Raman spectra of $As_{42}S_{58}$ thin films and bulk glass. _1:_ as-evaporated film, _2:_ exposed film, _3:_ annealed film, _4:_ bulk glass. The amplitudes of the curves 1-4 were normalized to the same value for the band 345 cm^{-1} (AsS_3 pyramids vibrations). For assignment see Fig. 2.

The process of photoinduced or thermally induced interaction of fragments can be described, e.g. in As-S films by a reaction

$$As_4S_4 + S_2 \rightarrow 2As_2S_3 \tag{2}$$

Such process was simulated in [8] considering that the as-evaporated chalcogenide film of As-S system is a solid solution (or molecular mixture) of As_4S_4, S_n and $(As_2S_3)_n$. The Raman spectra of such mixtures are similar to the spectra of as-evaporated films (Figs. 5-7, see also [8]). Comparing the intensities of individual bands, we were able to evaluate approximately the content of As_4S_4 in as-evaporated films of $As_{42}S_{58}$. This value is $\geq$ 20 mol.% [8]. Exposure, and even more annealing,

decreased the content of As_4S_4 molecules in films. In exposed films of $As_{42}S_{58}$, the content of As_4S_4 was decreased to $c(As_4S_4) \sim 10$-15 mol.%. In $As_{40}S_{60}$ and $As_{38}S_{62}$ films the amount of As_4S_4 is lower. It is interesting to note that according to Raman spectroscopy, the As_4S_4 molecules were found also in $As_{42}S_{58}$ bulk glasses (Figs. 5, 7) [8]. It does mean that the excess As in these As-rich glasses is partly in the form of As_4S_4 molecules.

Photoinduced effects were observed also in thin films of the Sb-S system (Figs. 8-10). The optical transmittance of as-evaporated films of Sb_2S_3 decreases after exposure (photodarkening). The exposure of as-evaporated Sb_2S_3 films is accompanied by a decrease of amplitude of the 165 cm^{-1} Raman band. This band (Fig. 10) can be assigned to Sb-Sb vibrations of S_3Sb-SbS_3 structural units [11]. As-evaporated films of Sb_2S_3 were evidently also dissociated during evaporation, and the films after evaporation are microheterogeneous, analogously to As_2S_3 films. The exposure accelerates the reactions between Sb-rich and S-rich parts of the film and the film becomes more homogeneous. The index of refraction of exposed (more homogeneous) films increases (Fig. 9), partly because of densification.
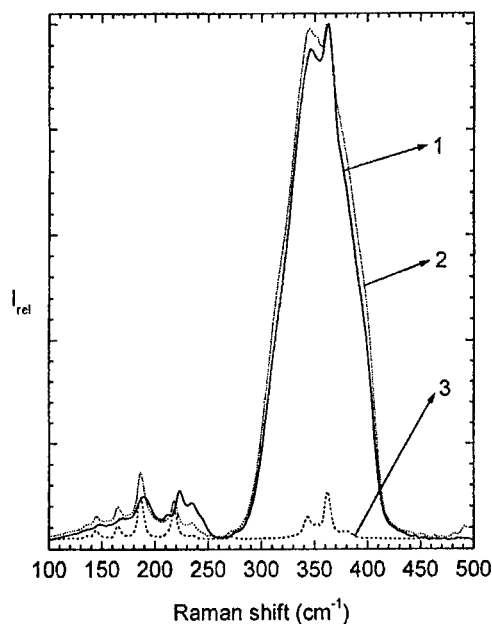

I_{rel}

100 150 200 250 300 350 400 450 500

Raman shift (cm^{-1})

Fig. 5. Reduced Raman spectra. *1*: $As_{42}S_{58}$ bulk glass, *2:* powdered mixture of 0.85 $As_{40}S_{60}$ glass + 0.15 As_4S_4 crystals, *3:* As_4S_4 crystals. The amplitudes of curves *1* and *2* were normalized to the same value for the band ~ 361 cm^{-1}. Amplitudes of As_4S_4 (curve *3*) were reduced to be comparable with curves *1* and *2*.

The analogous model, which was proposed for description of irreversible photoinduced effects in As-S systems ([8, 20, 29, 30], Eq. 3), can be probably applied for Sb-S system as well.

2. 2. Reversible photoinduced changes

In well-annealed films, the photoinduced changes of structure and optical properties due to exposure are often reversible. Annealing of exposed films can shift the film to the state before exposure. Annealed films of the As-S system, with a structure similar to glasses do not contain larger amounts of "fragments", e.g. of S_n and As_4S_4 (Figs. 2-4). They are evidently closer to thermodynamic equilibrium. The optically induced reactions among fragments (e.g. of the type of Eq. 2) do not play a role. Under exposure, the photolytic reactions in As-S films are more important, at least at room and lower temperatures [8]. At higher temperatures (close to the glass transition temperature, T_g, or above it), atoms or polyatomic fragments of structure are more mobile and they can react together to

eliminate the presence of photolytic products or lower their density. The system approaches the equilibrium by annealing.

The mechanism of *reversible* photoinduced changes still remains not fully clear in spite of the fact that strong evidence for structural atomic changes has been given [8,20,24,25]. Many authors (see e. g. [28]) generally accept that the photoinduced phenomena are connected with changes of local bonding configuration.
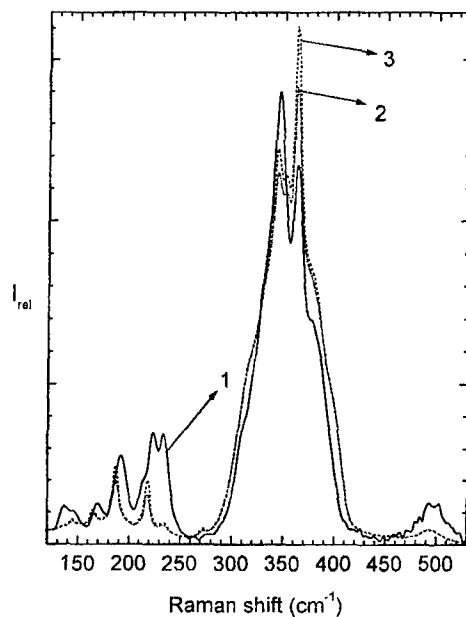

Fig. 6. Reduced Raman spectra. *1:* $As_{42}S_{58}$ as-evaporated film, *2:* mixture of powdered 0.85 $As_{40}S_{60}$ glass + 0.15 As_4S_4 crystals, *3:* mixture of powdered 0.8 $As_{40}S_{60}$ glass + 0.2 As_4S_4 crystals [8].

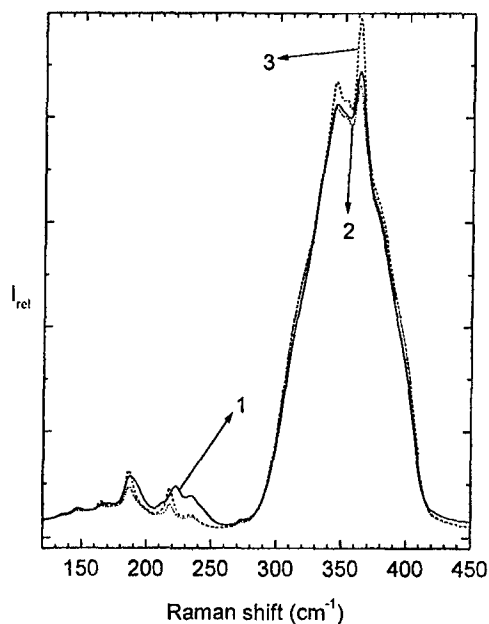Fig. 7. Reduced Raman spectra. *1:* $As_{42}S_{58}$ bulk glass, *2:* mixture of powdered 0.95 $As_{40}S_{60}$ glass and 0.05 As_4S_4 crystals, *3:* powdered mixture of 0.9 $As_{40}S_{62}$ glass and 0.1 As_4S_4 crystals.

The chemically simplest system, in which photoinduced effects were observed, is amorphous selenium. Kolobov found that, within the errors of experiment, there are nearly no photoinduced changes in coordination number of Se, but an increase in this number during photoexcitation was observed [19]. This increase means that the structure is changed during photoexcitation but without an invariable change of the coordination number after the light is off. The changes can proceed via changes of Se_8 rings to Se_n chains and vice versa (see, e.g. [17, 19]). In fact, in other systems, such as in the As-S system, the photoinduced phenomena are not connected with the changes of mean coordination number [20] but with changes of bond statistics, too.
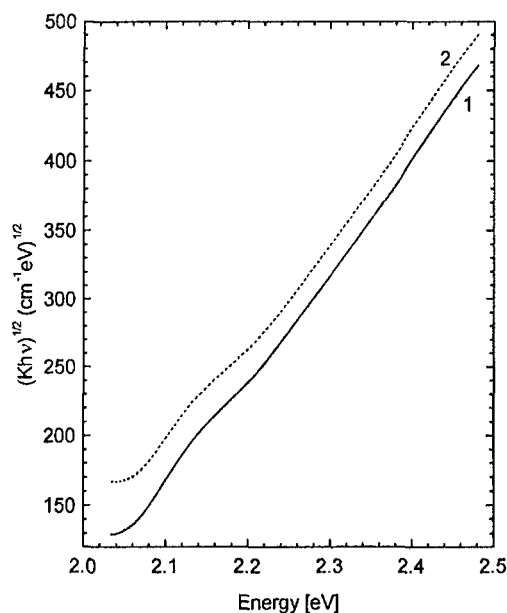

Fig.8. Absorption edge of thin film of Sb_2S_3.
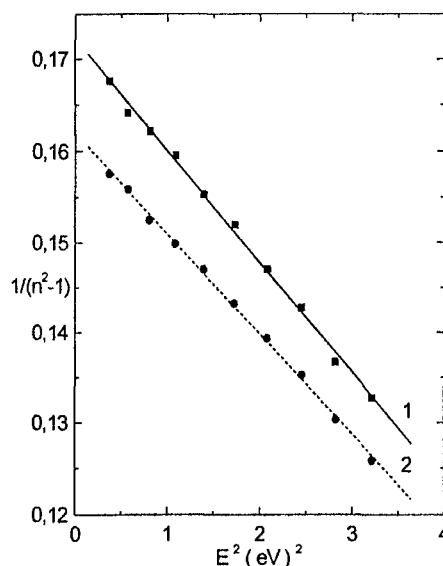1: as-evaporated film, 2: exposed film.

Fig. 9. Spectral dependence of $(n^2-1)^{-1}$ for thin films of Sb_2S_3. Then is index of refraction.
1: as-evaporated film, 2: exposed film.

Photoinduced changes of structure and of optical properties were found also in thin films of the As-Ga-S [7], in Ge-Sb-S [11, 31], and As-Sb-S system (Figs. 11, 12). The reversible part of changes of index of refraction is much stronger in $(As_2S_3)_{95}(Sb_2S_3)_5$ thin films than in pure As_2S_3 films of the same composition (Fig. 11). The reason is not clear up to now. Large irreversible changes of index of refraction were found also after exposure or after annealing of as evaporated films of $(As_2S_3)_{95}(Sb_2S_3)_5$ (irreversible changes).

Photoinduced changes in As_2S_3 containing Ga [7] are again accompanied by changes of intensities of Raman bands, which can be assigned to the vibrations of As-As bonds (235 cm^{-1}, Fig. 12). The amplitude of this band is enhanced after the exposure of annealed films. It is reduced after annealing. It does mean that not only the irreversible part of photoinduced effects, but also the reversible part is accompanied by changes of bond statistics and of structure in these amorphous systems, analogously as it was shown in pure As-S system [8, 20, 29-32].

For a description of reversible changes in As-S, As-Ga-S, As-Sb-S, and Sb_2S_3 films and bulk glasses, a model based on our earlier results of the study of a-As_2S_3 [20] is proposed. The exposure to light can shift the equilibrium of reaction (3) to the left- or right-hand side, depending on the composition and state of the sample, wavelength and intensity (Wcm^{-2}) of the light. Generally, a lower wavelength and larger intensity of light supports the photolysis (right-hand side direction), a lower energy and/or intensity can shift the reaction (3) to the left-hand side direction.

$$2|A-B| \xrightarrow{hv_i, I_i} |A-A| + |B-B|. \tag{3}$$
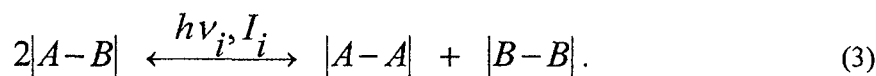
The |A-B| in Eq. 3 is a chemical bond between atoms A and B, v_i and I_i are frequencies and intensities of incident light. Increasing frequency and/or intensity shifts the equilibrium of the reaction (3) to the right hand side, lowering of energy or intensity of incident light or annealing of sample shifts the equilibrium of Eq. 3 to the left hand side.

Reaction (3) proceeds not only in thin films, but also in bulk samples and glassy powders, both stoichiometric and non-stoichiometric as confirmed by Raman spectroscopy [8]. The formation of As-As bonds due to exposure of As_2S_3 was confirmed recently by Uchino et al. [34], based on ab-initio molecular orbital calculations.

It was found earlier that the mechanisms described by Eq. (3) could be applied also for Ge-Sb-S glasses and films [11, 31].
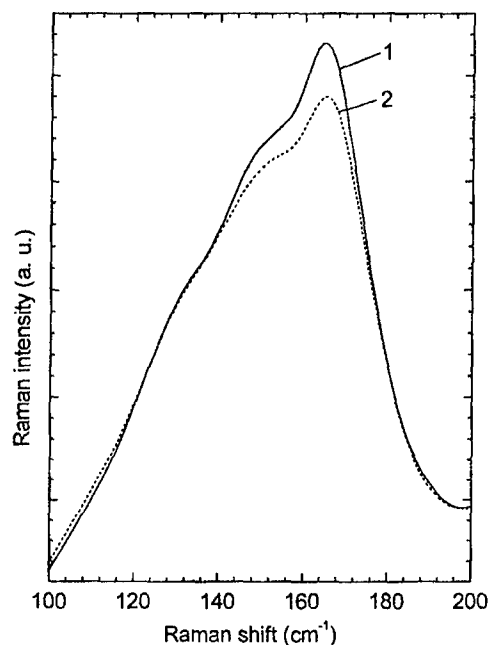

Fig. 10. Reduced Raman spectra of Sb_2S_3 film. *1:* as-evaporated film, *2:* exposed film. The band near 165 cm^{-1} corresponds to S_3Sb-SbS_3 vibration modes. The spectra were normalized to the equal amplitude of the band near 303 cm^{-1} which corresponds to the SbS_3 pyramids vibrations. The density of such structural units is prevailing in the structure of evaporated Sb_2S_3 films and it is considered that their density is constant during the exposure.

It is now generally accepted that both irreversible and reversible photoinduced changes are connected with structural changes of amorphous films and glasses. We have shown without any doubt, that in many above mentioned systems an important role is played by photochemical reactions among fragments of amorphous films (irreversible changes) or by photolytic reactions mainly in annealed films and bulk glasses (reversible changes). The other possibilities e.g. over-coordinated or under-coordinated structural entities (atoms, defects) can also play a role (see, e.g. [34] and papers cited), but there were found only small changes of the mean coordination numbers [19] of different atoms in amorphous films. The photoinduced changes of structure (excluding crystallization and amorphization) are generally small, only a small part of all atoms changes probably their positions and chemical partners. As a result, the experimental evidence of structural changes is often non-persuading (see, e. g. [20]) and several (partly speculative) models can be applied. We believe, that many under-coordinated and over-coordinated defects are only intermediate ones and the system becomes stabilized by change of chemical bonds statistics to approach chemical equilibrium.
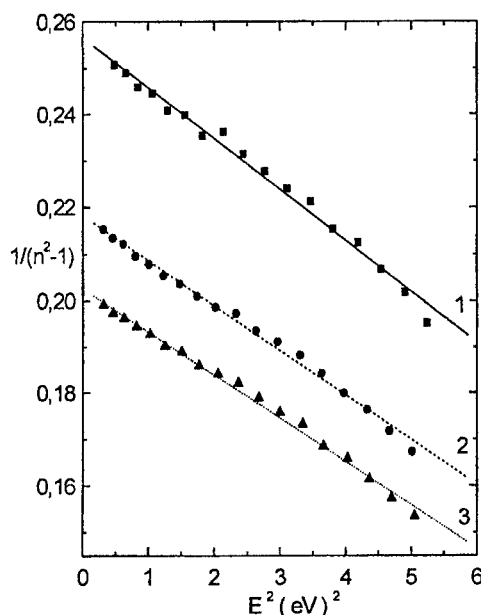
Fig.11. Spectral dependence of $(n^2-1)^{-1}$ for $95As_2S_3.5Sb_2S_3$. The n is index of refraction.
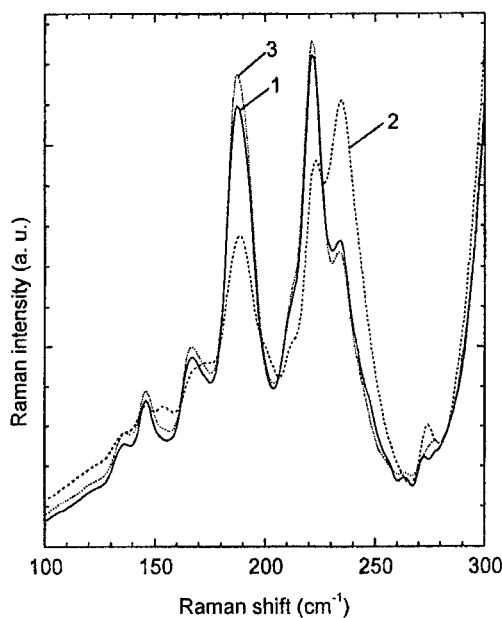*1:* as-evaporated film, *2:* exposed film, *3:* annealed film.

Fig. 12. Reduced Raman spectra of thin films (d = 1000 nm) of $95As_2S_3.5GaS$. *1:* annealed film, *2:* film exposed after annealing, *3:* film was annealed after exposure. The change of amplitude corresponds to reversible structural changes, the band (235 cm^{-1}) with increased amplitude corresponds to As-As vibrations [7, 20].

All changes of local structure or state of samples are accompanied by changes of physico-chemical properties, such as optical transmittivity and reflectivity, index of refraction, and chemical reactivity (see, e.g. Figs. 1, 8, 9, 11, and [7-12, 20, 29-32]. The changes of physicochemical properties, e.g. the "photodarkening" can be modeled. A similar shift of absorption edge can be received by change of composition in mixtures of supposed components of the glass or of the amorphous film. Similar shift can be received in mixtures of supposed photochemical products [8]. All photoinduced changes are dependent on the composition, state of the samples, temperature, intensity and wavelength of the exciting light [8, 20, 29-32]. Some of these changes are large enough to be applied (presently or potentially) in optics, electronics and optoelectronics.

3. Applications

Chalcogenide films are contrary to oxide films, transparent in the near- or mid-infrared region of the spectrum (~ 0.8 – 12 µm), and they can be used for applications in this region. The refractive index of chalcogenides is larger in the near- and mid- infrared region (typically from 2.2-2.9) then in silica and silicates; chalcogenides can match with high refractive index materials, such as Si, GaAs, ZnSe, InSb and others.

Photoresists of large size (areas) can be prepared by vacuum evaporation and very high resolution of 5000-10000 lines/mm can be obtained after their exposure [29, 30, 35]. The resolution capability of chalcogenide films can be further increased to sub-wavelengths region by near – field optical technique [35, 36]. Nano-writing is then possible (e.g. 125 nm lines were obtained [35]). In this case and in similar ones, the sensitivity can be increased by several orders when short pulses are used (see e. g. Ref. [37] and papers cited in) instead of continuous-light exposure. This effect is not fully understood; some local heating, which enables changes of atomic positions and possibly also non-linear effects, or two-photon excitation, could produce such effects.

For some pattern production, e.g. for IR gratings production, deep etching is necessary. Sharp edges with height up to 5-10 µm were obtained (see, e.g. [38, 39]). The etching solutions for As chalcogenides are based on alkylamines or on other alkaline solutions; pure, or such solutions containing surface-active additives, are applied [33, 39]. Solutions containing H_2O_2 are used for Ge-chalcogenide based photoresists [40]. The contrast obtained after etching can be very high (with sharp edges). It can be also very gentle or low, and gray tones or gray scale can be achieved by variation of exposure and etching conditions [37].
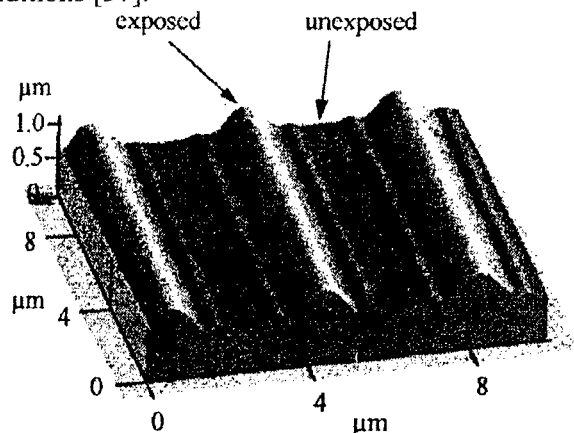

Fig. 13. Grating produced by exposure through a mask by cw-light of wavelength 364 nm [33].

The exposure can change also the volume and surface profile – the exposed parts often have larger volume and gratings and micro-lenses were prepared (Fig. 13, [10, 40]). Micro-lenses or micro-lens arrays can be fabricated from photoresists of As-Se and As-S systems [36, 41] by exposure through a mask with microhole(s). Lenses with focal length several tens of µm and diameter of several microns can be produced [19]. Spherical microlenses can be also prepared. The optical image of the patterns is often directly visible after exposure. Such microlenses can be applied in CCD cameras, imaging machines, optical communication and in IR technology.

Part of the changes of index of refraction due to exposure, e.g. of As chalcogenides, can be ascribed to changes of the volume (photoinduced expansion, density change). The atomic model is analogous [37] to that given in papers [20, 31] for As-S and Ge-Sb-S systems.

It was already mentioned that sub-band gap writing is also possible. In this case, the absorption of light in band tails in the optical gap plays a role. Such tails in films and glasses are formed mainly by fluctuations in bond angles and lengths. The exposure can change the local structure (including bond angles and lengths), the optical transmittivity and the index of refraction. As a result, the sub-band -gap exposure can be applied for holographic recording (e.g. in amorphous As_2S_3 films at room temperature [42]). The photoinduced effect under these conditions has some different features: the changes are not permanent and the thickness of the films is not changed. Sub-band-gap illumination strongly decreases also the viscosity of As_2S_3 glass, which is apparently caused by excitation of weaker or Van der Waals bonds connecting some blocs in the glass structure [40, 41].

A very promising application of photoinduced effects in chalcogenide amorphous films is connected with optical storage. Some of these effects in ternary tellurides are already applied for optical discs (the change from amorphous to crystalline state and vice versa) with a capacity of several Gb per disk [44, 45]. The optically induced crystallization or amorphization can be observed in many binary systems such as As-Se, As_2S_3, Sb_2S_3, Sb_2Se_3, Sb_2Te_3 [36, 43] and in many ternary tellurides [44-51] and selenides [52]. Both thermal and photoinduced effects, or their combination, are apparently behind such effects. When compared with the hole-burning methods that usually use thin metal films, the crystallization – amorphization process needs lower laser power and can be in principle reversible. The threshold power necessary for such a transition (crystallization) is from 100 - 200 W/cm^2 for Sb_2S_3, Sb_2Se_3 and Sb_2Te_3 films. The lowest threshold power was found for Sb_2S_3 [45]. The photoinduced changes of optical properties can have also a deteriorating effect on optical elements and such changes are undesirable. They can lower the performance of fibers or of optical elements as noticed in many materials, e.g. in Ge-Ga-S glass [41], which are used as hosts for rare-earth ions with a relatively intense luminescence in the near – infrared region and can be applied for light generation and amplification. Exposure by UV light causes a red shift of the absorption edge and lowers the transmission of the material. The crystallization can also lower the transmittance of optical elements. In such cases, lower light intensities, longer wavelengths of light, or materials with negligible photoinduced effects have to be used.

4. Conclusion

Photoinduced effects in chalcogenide amorphous systems are still not fully clear in spite of the fact that many of them are already applied or can be applied in the future. It was shown that an important part of photoinduced changes of structure is accompanied by changes of chemical bond statistics and by changes of atomic structure. Further materials and effects are studied in order to elucidate the photoinduced effects.

For application of these effects we are at the beginning and many new materials are studied in order to find systems with new or better properties for current or future applications, which are at present evidently far from the optimal state.

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